

New initiative

Aluminum-based drinking-water treatment residuals: A novel sorbent for perchlorate removal

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Received 3 July 2005; received in revised form 12 August 2005; accepted 13 August 2005

Drinking-water treatment residuals are a low-cost sorbent for perchlorate.

Abstract

Perchlorate contamination of aquifers and drinking-water supplies has led to stringent regulations in several states to reduce perchlorate concentrations in water at acceptable levels for human consumption. Several perchlorate treatment technologies exist, but there is significant cost associated with their use, and the majority of them are unable to degrade perchlorate to innocuous chloride. We propose the use of a novel sorbent for perchlorate, i.e. an aluminum-based drinking-water treatment residual (Al-WTR), which is a by-product of the drinking-water treatment process. Perchlorate sorption isotherms (23 ± 1 °C) showed that the greatest amount (65%) of perchlorate removed by the Al-WTR was observed with the lowest initial perchlorate load (10 mg L^{-1}) after only 2 h of contact time. Increasing the contact time to 24 h, perchlorate removal increased from 65 to 76%. A significant correlation was observed between the amounts of perchlorate removed with evolved chloride in solution, suggesting degradation of perchlorate to chloride.

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Keywords: Perchlorate; Chloride; Drinking-water treatment residuals; Adsorption; Desorption

1. Introduction

Perchlorate (ClO_4^-) is an emerging inorganic contaminant that has only recently been charged with severe human health effects, such as thyroid hormone and neurodevelopment disruption, especially in infants and pregnant women (Urbansky, 1998). Its toxicity is the result of the inhibition of iodide uptake, possibly leading to reduced production of thyroid hormone. Even minimal levels of perchlorate uptake by the thyroid gland can cause severe dysfunctions in the production of thyroid hormones, leading to cancer development (Tonnachera et al., 2004). Current data suggest that $4\text{--}18 \text{ } \mu\text{g L}^{-1}$ is an acceptable exposure level but maximum contaminant levels for perchlorate vary from state to state. Based on a preliminary

toxicity assessment, the draft estimate of the U.S. Environmental Protection Agency for a future regulatory limit of perchlorate in drinking water is $1 \text{ } \mu\text{g L}^{-1}$.

Sources of perchlorate are mostly anthropogenic. Ammonium and potassium perchlorate salts have been traditionally used as an additive and oxidant, respectively, in missile/rocket propellants and fireworks. Perchlorate salts are also used in the manufacture of automotive airbag inflators, as a mordant for fabrics and dyes, and in the production of paints and enamels (Moore et al., 2003). Improper disposal of perchlorate-containing waste has resulted in widespread contamination of groundwater and drinking-water supplies in the United States (Damian and Pontius, 1999). Tons of perchlorate-containing ammunition waste (demilitarization of weaponry) has been repeatedly disposed off in soils, resulting in significant perchlorate leaching through the vadose zone to the groundwater.

Several treatment technologies exist for the removal of perchlorate from contaminated aquifers, soils, and drinking-water

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supplies. Ion exchange using mono- or bi-functional resins has been identified as one of the most promising methods for removing low levels of ClO_4^- (Gu et al., 2005), but interferences by other anions such as sulfate on the effectiveness of perchlorate removal might limit the performance of this treatment technology. Use of zero valent iron particles seems advantageous to ion exchange because of their ability to destroy perchlorate by sorption and subsequent chemical reduction to chloride (Moore et al., 2003).

Elevated cost associated with the use of the above treatment technologies can be prohibitive for small communities or developing countries, striving to produce free-from-perchlorate potable and irrigating water. In this preliminary report, we propose the use of aluminum-based drinking-water treatment residuals (Al-WTRs) as an effective, yet highly economical novel sorbent for perchlorate. The Al-WTRs can be obtained free-of-charge from drinking-water treatment plants. These byproducts of the water treatment process are physical mixtures of either Fe or Al hydr(oxides) or CaCO_3 that also contain sediment, and small quantities of activated carbon, and/or polymer. Addition of Fe, Al, or Ca salts to raw water removes colloids, color, sediment and contaminants from surface and groundwater supplies intended for potable water use. Previous research by the authors has shown that WTRs are porous particles with high internal surface area (Makris et al., 2004). Upon hydration of WTR particles, absorption of water and solutes into the internal pore network would result in physical sorption of perchlorate. We also hypothesized that the high aluminum oxide and organic carbon content of the Al-WTR could promote perchlorate degradation and subsequent formation of innocuous chloride.

The primary objectives of the reported study were (i) to demonstrate the use of an Al-based WTR as an effective sorbent for perchlorate, and (ii) to investigate the potential of perchlorate degradation in the presence of the Al-WTR surface rich in aluminum oxide and organic carbon.

2. Materials and methods

The Al-WTR was obtained from the drinking-water treatment plant in Bradenton, Florida. Additions of alum and a small amount (0.17 mg L^{-1}) of a copolymer of sodium acrylate and acrylamide during water treatment resulted in production of the Al-WTR. The WTR particles were allowed to air-dry, and were subsequently passed through a 1-mm sieve prior to their use in any experiment.

General chemical characterization of the Al-WTR from Bradenton, FL has been reported elsewhere (Makris et al., 2004). In brief, pH was measured in a 1:2 (w:v) aqueous suspension, and soluble reactive P concentration was measured in a 0.01 M KCl solution at a 1:10 (g:mL) solid:solution ratio after 10 d of reaction. Total C and N were determined by combustion at 1010°C using a Carlo Erba NA-1500 CHNS analyzer. Total-recoverable P, Fe, and Al were determined by inductively-coupled plasma mass spectroscopy (ICP-MS) following digestion according to the EPA Method 3050B (USEPA, 2000). Oxalate-extractable P, Fe, and Al were determined by ICP-MS after extraction at a 1:60 (g:mL) solid:solution ratio, following the procedures of McKeague et al. (1971).

Perchlorate sorption capacity of the Al-WTR was determined in batch equilibration. NaClO_4 (KR Grade, Aldrich, USA) was used as the source of perchlorate in all experiments. WTR samples were reacted with inorganic perchlorate in 1:5 (g:mL) WTR:0.01 M KCl solutions at initial perchlorate

concentrations of 10, 50, 100 and 200 mg L^{-1} for 1, 2, 24, and 96 h at $23 \pm 1^\circ\text{C}$. Test tubes were purged with N_2 gas and were capped immediately. Following a specific shaking period (at 120 rpm), the tubes were centrifuged (3000g), filtered, and analyzed for perchlorate and chloride by ion chromatography (Dionex 500, Dionex, Sunnyvale, CA, USA). An IonPac AS16 analytical ($4 \times 250 \text{ mm}$) and an IonPac AG16 guard column ($4 \times 50 \text{ mm}$) were used to separate perchlorate from the other anions present in solution.

After sorption, the supernatant was removed and WTR-containing tubes were filled with 5 mL deionized water to evaluate perchlorate desorption from the Al-WTR. Suspensions were reacted for 1, 2, 24, and 96 h, and the amount of perchlorate desorbed was calculated as the difference between perchlorate sorbed and perchlorate measured in solution after the desorption step.

3. Results and discussion

3.1. General chemical properties of the Al-WTR

Physicochemical properties for the Al-WTR were similar to those of another batch of the same Al-WTR reported elsewhere (Makris et al., 2004) (Table 1). In brief, total Al and C concentrations were high and typical of Al-WTRs produced nationally. Oxalate-extractable Al values were close to total Al concentrations (75% of total Al) consistent with the amorphous nature of the Al-WTR, since oxalate-extractable P, Fe, and Al are usually associated with the non-crystalline phase of metal oxides (McKeague et al., 1971). The Al-WTR was slightly acidic in nature (Table 1). Potential release of metals from the WTRs was addressed using the toxicity characteristic leaching procedure (TCLP) test. The TCLP values for As in the Al-WTR were well below the hazardous waste toxicity characteristic criterion (5 mg L^{-1}) as defined in Title 40 of the Code of Federal Regulations (CFR), Part 261.24 (Table 2). Similarly, TCLP values for several other metals (Pb, Zn, Cu, etc.) were well below the threshold values that would classify the WTR as hazardous waste (Table 2), thus, permitting WTR land application as an environmentally sound disposal method.

3.2. Perchlorate sorption by the Al-WTR

Sorption experiments (23°C) showed that the Al-WTR had high affinity for perchlorate (Fig. 1). Batch experiments with control (no WTR particles) perchlorate solutions revealed no sorption of perchlorate to tube walls since perchlorate recovery was $100 \pm 5\%$. The greatest amount (65%) of perchlorate removed by the Al-WTR was observed with the lowest initial perchlorate load (10 mg L^{-1}) after only 2 h of contact time. By increasing the contact time to 24 h, perchlorate removal at the lowest initial perchlorate concentration increased from 65 to 76% (Fig. 1). Perchlorate removal decreased from 75 to

Table 1
General chemical properties of the Al-WTR obtained from Bradenton, FL

Source	pH	KCl-P (mg kg^{-1})	C (g kg^{-1})	N (g kg^{-1})	Total (g kg^{-1})			Oxalate (g kg^{-1})		
					P	Fe	Al	P	Fe	Al
Al-WTR	6.1 ^a	6.1	188	4.5	3.5	12.2	110.0	3.0	5.7	82.3

^a The results are the mean of 2 measurements.

Table 2
Toxicity characteristic values of several metals and metalloids measured in the Al-WTR, using the TCLP extraction method

Analyte	mg L ⁻¹
Cr	<0.0084 ^a
Ni	<0.0810
Cu	<0.0468
Zn	<0.0027
Ag	<0.0110
Pb	<0.0546
S	64.3
Cd	<0.0083
B	<0.1172
K	4.64
Ti	<0.0027
Mn	0.41
Ca	36.53
Co	<0.0087
Mg	6.87
As	<0.0253
Se	0.75
Ba	0.34
W	0.29
Hg	0.55

^a ICP-AES instrument detection limits.

31% with increasing initial perchlorate in solution (from 10 to 200 mg L⁻¹) after 24 h (Fig. 1). Using zerovalent iron particles, Moore et al. (2003) were able to remove 66% perchlorate in 336 h in their highest dosage system (0.4 g mL⁻¹). Our preliminary perchlorate removal capacity by the Al-WTR seems comparable to the data obtained by Moore et al. (2003).

Immediately following the sorption step, perchlorate desorption experiments using d-H₂O were initiated. The amount of perchlorate desorbed was expressed as percentage of the amount previously sorbed, which was always <2% (Table 3). There was no significant effect of time (1–24 h) or sorbed perchlorate concentration on desorption of perchlorate with d-H₂O from the Al-WTR particles. The inability of d-H₂O to desorb from the WTR particles suggests hysteretic adsorption, hence, stable immobilization of perchlorate by the Al-WTR. Minimal desorption of perchlorate from anion

Table 3
Desorbed perchlorate with d-H₂O from the Al-WTR, Bradenton as a function of desorption time and initial perchlorate concentration added

Initial ClO ₄ ⁻ added (mg L ⁻¹)	Desorbed ClO ₄ ⁻ (% sorbed)		
	1 h	2 h	24 h
10	1.8	1.7	1.3
50	1.7	0.5	1.7
100	0.7	0.1	1.6
200	1.5	1.2	0.1

exchange resins was observed using 10 mM HCl in column experiments elsewhere (Gu et al., 2005); results obtained from this study using Al-WTR are comparable to the data obtained by Gu et al. (2005). These encouraging preliminary data suggest the potential of Al-based WTRs for use in the field as permeable reactive barriers where contaminated water flows through WTR packed particles.

3.3. Effect of shaking time and chloride evolution

Kinetics of perchlorate sorption by the Al-WTR was an important consideration in the overall magnitude of perchlorate sorption. There was no significant difference in the amount of perchlorate removed between 1 and 2 h of shaking time, but perchlorate removal significantly increased after 24 h at all initial perchlorate concentrations (10, 50, 100 or 200 mg L⁻¹) (Fig. 1). Perchlorate removal further increased as the system was allowed to react for 96 h. However, the rate of perchlorate removal decreased for times >24-h sorption and with increasing initial perchlorate concentrations, suggesting a potential diffusion-limited sorption into the internal sites of the WTR. Previous work with another batch of the same Al-WTR showed that the overall sorption of phosphorus was diffusion-limited into the micropores of the WTR (Makris et al., 2004). The significant internal pore network of the material could be posing steric hindrance to perchlorate diffusion into the particles. Further spectroscopic work is needed to support the speculation on diffusion-limited perchlorate sorption.

Chloride concentrations in solution were also monitored during the kinetic experiments to evaluate the potential of perchlorate degradation to chloride on WTR surfaces. Upon perchlorate addition, Cl⁻ concentrations in solution were greater than those in control samples at all reaction times, indicating Cl⁻ generation in the reaction system (data not shown). There was no significant relationship between the amounts of perchlorate removed with Cl⁻ concentrations measured in solution after 1 or 2 h of reaction (Fig. 2). However, there was a significant ($p < 0.001$) linear correlation ($r^2 \geq 0.95$) between the amount of perchlorate removed with evolved Cl⁻ in solution after reaction for 24 or 96 h (Fig. 2). This might indicate degradation of perchlorate to chloride in the presence of aluminum oxide, which serves as a proton donor that promotes hydrodechlorination (Lien and Su, 2004). Alternatively, it might also suggest chemical reduction of perchlorate to chloride using organic matter as the electron source. Neither hypothesis

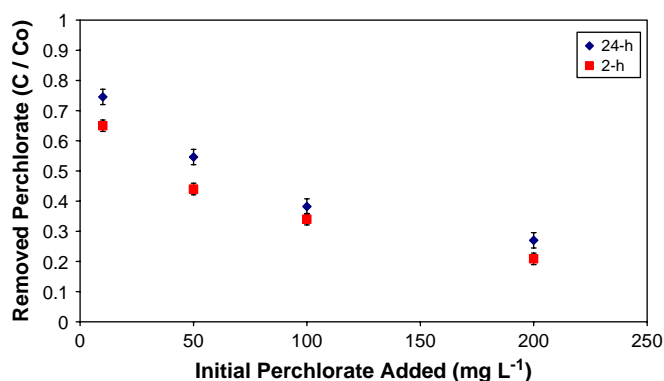


Fig. 1. Perchlorate removal (23 °C) by the Al-WTR from different initial perchlorate aqueous solutions at two different contact times. Data are presented as the mean and a standard deviation of two replicates.

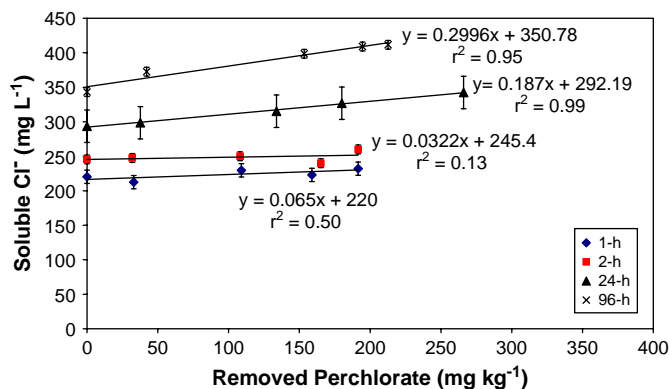


Fig. 2. Relationship of removed perchlorate and the amount of soluble chloride evolved from the Al-WTR surfaces at different contact times. The positive linear relationship holds for 24 and 96 h, but not for 1- or 2-h period, suggesting kinetically-driven perchlorate degradation. Data are presented as the mean and a standard deviation of two replicates.

could be verified until further investigations are performed. The excellent correlation between released Cl^- with the amount of perchlorate removed after 24 or 96 h, and not with the amount removed after 1 or 2 h indicates the possibility of perchlorate degradation into the porous network of the Al-WTR.

Preliminary data obtained from the reported study suggests that aluminum-based WTR could be a promising, cost-effective sorbent for perchlorate in contaminated water, or perchlorate-containing ammunition wastes. Physical sorption of perchlorate by the Al-WTR followed by possible chemical reduction to chloride allows for no further treatment of spent WTRs previously used for perchlorate removal. Further studies with Al-WTRs from different drinking-water treatment plants are needed to confirm the observed preliminary trends; on-going

studies in our laboratory aim in maximizing perchlorate sorption by the Al-WTRs.

Acknowledgments

The authors would like to thank the drinking-water treatment plant in Bradenton, FL for providing the WTR samples.

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